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(21)Application number : 11-016423 (71)Applicant : TECHNO POLYMER KK  
(22)Date of filing : 26.01.1999 (72)Inventor : ITO HIROYUKI  
NORO MASAHIKO

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### (54) THERMOPLASTIC RESIN COMPOSITION FOR LASER MARKING

#### (57)Abstract:

PROBLEM TO BE SOLVED: To obtain a thermoplastic resin composition for laser marking, having excellent color development of laser marking, improved practical impact resistance and chemical resistance.

SOLUTION: This composition features compounding (A) 100 pts.wt. of a thermoplastic resin component composed of 50-100 wt.% of a rubber reinforced resin (A-1) subjected to graft polymerization with a small amount of a (meth) acrylic ester and 50-0 wt.% of a copolymer (A-2) copolymerized with a specific amount of a vinyl cyanide compound as main components and containing a specific amount of a polymerized vinyl cyanide compound with (B) 0.01-5 pts.wt. of a black-based compound such as carbon black.

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## CLAIMS

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[Claim(s)]

[Claim 1] (A) Rubber-like polymer (a) Under 5 - 30% of the weight of existence, acrylic ester (meta) (b)45-70 % of the weight, at least one sort of monomer (component c) 0-50 % of the weight chosen from the group of an aromatic series vinyl compound, a vinylcyanide compound, an acid-anhydride system compound, and a maleimide system compound -- [ -- however (a) 50 - 100 % of the weight (A-1) of rubber strengthening resin obtained by carrying out the polymerization of +(b)+(c) = 100-% of the weight], 35 - 50 % of the weight of vinylcyanide compounds, an aromatic series vinyl compound, acrylic ester (meta), 50 - 0 % of the weight (A-2) of copolymers obtained by carrying out the polymerization of 65 - 50 % of the weight of at least one sort of monomer components chosen from the group of an acid-anhydride system compound and a maleimide system compound -- [ -- however As opposed to the thermoplastics component 100 weight section which uses (A-1)+(A-2) = 100-% of the weight] as a principal component, and contains the amount of vinylcyanide compounds by which the polymerization was carried out one to 33% of the weight (B) Thermoplastics constituent for laser marking characterized by blending the black system compound 0.01 - 5 weight sections.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the thermoplastics constituent for laser marking which comes to blend black system compounds, such as carbon black, with a thermoplastics constituent.

[0002]

[Description of the Prior Art] If laser light is irradiated conventionally at the resin ingredient which blended the compound of a black system of a certain kind with thermoplastics, an exposure part's being black or the technique colored white is known (the Siemens application, the Japanese Patent Publication No. No. 59663 [ 62 to ] official report). Such a laser marking technique is used for alphabetic character printing of OA equipment panels, such as key printing of a keyboard, and FAX, etc., compared with

TAMPO printing used conventionally, is low cost and very excellent in respect of the endurance of an alphabetic character etc. However, the chemical resistance to the sweat of a hand, a cleaning agent, a detergent, a hair liquid, a hand cream, etc. was inferior in the thermoplastics ingredient for old laser marking, and the problem that the keyboard which used the laser marking technique breaks at the time of use has produced it. Moreover, shock resistance (practical use shock resistance) is also inferior in the conventional resin constituent for laser marking.

[0003]

[Problem(s) to be Solved by the Invention] This invention was made against the background of the technical problem of the above-mentioned conventional technique, solves the above-mentioned trouble, and aims at offering the thermoplastics constituent for laser marking which raised chemical resistance and practical use shock resistance.

[0004]

[Means for Solving the Problem] this invention -- the shape of (A) rubber -- the bottom of (Polymer a) 5-30 % of the weight existence -- acrylic ester (meta) (b) -- 45 to 70% of the weight at least one sort of monomer (component c) 0-50 % of the weight chosen from the group of an aromatic series vinyl compound, a vinylcyanide compound, an acid-anhydride system compound, and a maleimide system compound -- [ -- however (a) 50 - 100 % of the weight (A-1) of rubber strengthening resin obtained by carrying out the polymerization of +(b)+(c) = 100-% of the weight], 35 - 50 % of the weight of vinylcyanide compounds, an aromatic series vinyl compound, acrylic ester (meta), 50 - 0 % of the weight (A-2) of copolymers obtained by carrying out the polymerization of 65 - 50 % of the weight of at least one sort of monomer components chosen from the group of an acid-anhydride system compound and a maleimide system compound -- [ -- however As opposed to the thermoplastics component (henceforth "(A) thermoplastics component") 100 weight section which uses (A-1)+(A-2) = 100-% of the weight] as a principal component, and contains the amount of vinylcyanide compounds by which the polymerization was carried out one to 33% of the weight (B) The thermoplastics constituent for laser marking characterized by blending the black system compound 0.01 - 5 weight sections is offered.

[0005]

[Embodiment of the Invention] (A) thermoplastics component used for this invention is a convention \*\*\*\*\* thing about the amount of vinylcyanide compounds by which used as the principal component the copolymer (A-2) which specified the amount of copolymerization of the rubber strengthening resin (A-1) which specified the amount of copolymerization of acrylic ester (meta) (b) or this rubber strengthening resin (A-1), and a vinylcyanide compound, and the polymerization was carried out into. (\*\* A) thermoplastics component.

[0006] The above-mentioned rubber strengthening resin (A-1) is rubber strengthening resin obtained under existence of a rubber-like polymer (a) by carrying out the polymerization of the above-mentioned monomer component (b) and the (c). As the above-mentioned rubber-like polymer (a), polybutadiene, polyisoprene, Butadiene Styrene, Butadiene

Acrylonitrile, An ethylene-propylene-(nonconjugated diene) copolymer, an ethylene-butene-1 (nonconjugated diene) copolymer, An isobutylene-isoprene copolymer, acrylic rubber, a styrene-butadiene-styrene block copolymer, Hydrogenation diene system (block, random, and gay) polymers, such as a styrene-butadiene-styrene radial tele block copolymer, a styrene-isoprene-styrene block copolymer, and SEBS, a polyurethane rubber, silicone rubber, etc. are mentioned. In these, polybutadiene, Butadiene Styrene, an ethylene-propylene-(nonconjugated diene) copolymer, an ethylene-butene-1-(nonconjugated diene) copolymer, a hydrogenation diene system polymer, and silicone rubber are desirable.

[0007] In addition, if graft decussation agents (for example, a thing, gamma-methacryloxypropylmethyldimethoxysilane, etc. containing a vinyl group) are used 0.01 to 10% of the weight into silicone rubber when using silicone rubber for a rubber-like polymer (a), the thermoplastics constituent for laser marking which is excellent also in shock resistance and sliding nature will be obtained. Moreover, if two or more sorts of rubber-like polymers (a) with which rubber particle size differs are used, the thermoplastics constituent for laser marking of this invention which is excellent in shock resistance and physical-properties balance will be obtained further. It is desirable to use the rubber-like polymer (a) with which two sorts of particle size, 80-180nm and about 180-480nm, differs as a desirable particle size. In this case, even if it carries out the polymerization of a monomer component (b) and the (c) under two sorts of existence of a rubber-like polymer (a), two sorts of rubber strengthening resin (A-1) with which rubber particle size differs can also be used.

[0008] As the above and acrylic ester (meta) (b), a methyl acrylate, an ethyl acrylate, butyl acrylate, a methyl methacrylate, ethyl methacrylate, methacrylic-acid butyl, etc. are mentioned. In these, a methyl methacrylate and butyl acrylate are desirable. This (meta) acrylic ester (b) is a component indispensable to laser marking coloring of this invention, and the amount of copolymerization in rubber strengthening resin (A-1) is 55 - 63 % of the weight still more preferably 50 to 65% of the weight preferably 45 to 70% of the weight. Laser marking nature is inferior in it being less than 45 % of the weight, and on the other hand, when it exceeds 70 % of the weight, thermal resistance and chemical resistance are inferior.

[0009] The above-mentioned monomer components (c) are at least one sort of monomers chosen from the group of an aromatic series vinyl compound, a vinylcyanide compound, an acid-anhydride system compound, and a maleimide system compound. A monomer component (c) can use together one-sort independence or two sorts or more. As an aromatic series vinyl compound which constitutes the above-mentioned monomer component (c), chlorination styrene, such as bromination styrene, such as styrene, alpha methyl styrene, o-methyl styrene, m-methyl styrene, p-methyl styrene, vinyltoluene, alpha-ethyl styrene, methyl-alpha methyl styrene, dimethyl styrene, bromostyrene, dibromo styrene, and TORIBUROMO styrene, chloro styrene, dichloro styrene, and TORIKURORO styrene, styrene sulfonic-acid sodium, etc. are mentioned. In these,

styrene, alpha methyl styrene, and p-methyl styrene are desirable.

[0010] Moreover, acrylonitrile, a methacrylonitrile, etc. are mentioned as a vinylcyanide compound which constitutes the above-mentioned monomer component (c). In these, acrylonitrile is desirable.

[0011] Furthermore, a maleic anhydride etc. is mentioned as an acid-anhydride system compound which constitutes the above-mentioned monomer component (c). furthermore, as a maleimide system compound which constitutes the above-mentioned monomer component (c) Maleimide, N-methyl maleimide, N-ethyl malei mide, N-propylmaleimide, N-isopropylmaleimide, N-lauryl maleimide, N-phenyl maleimide, N-(2-methylphenyl) maleimide, N-(2, 6-diethyl phenyl) maleimide, N-(4-carboxyphenyl) maleimide, N-(4-hydroxyphenyl) maleimide, N-(4-BUROMO phenyl) maleimide, TORIBUROMO phenyl maleimide, N-(4-chlorophenyl) maleimide, N-cyclohexyl maleimide, etc. are mentioned. In these, N-phenyl maleimide is desirable. In addition, if the above-mentioned maleimide system compound is copolymerized 30 to 60% of the weight in a monomer component (c), the thermal resistance of the thermoplastics constituent for laser marking of this invention will improve. When the content of the above-mentioned maleimide system compound component exceeds 60 % of the weight, laser marking nature is inferior.

[0012] The preparation presentation at the time of carrying out the graft polymerization of acrylic ester (meta) (b) and the monomer component (c) to the above-mentioned rubber-like polymer (a) (a) 30% of the weight a component 5 the (b) component 45 - 0 - 50 % of the weight of 70-% of the weight and (c) components preferably (a) They are a component 15 the (b) component 55 - 25 - 30 % of the weight of 60-% of the weight and (c) components 25% of the weight [however, (a)+(b)+(c) =100 % of the weight]. (a) Shock resistance is not enough in a component being less than 5 % of the weight, and if it, on the other hand, exceeds 30 % of the weight, the fall of a poor appearance and fabrication nature generates and is not desirable. Moreover, laser marking nature is inferior in the amount of copolymerization of the (b) component being less than 45 % of the weight, and on the other hand, when it exceeds 70 % of the weight, chemical resistance and shock resistance are inferior. Furthermore, when the amount of copolymerization of the (c) component exceeds 50 % of the weight, laser marking nature is inferior.

[0013] Moreover, the rate of a graft of rubber strengthening resin (A-1) is 20 - 70% especially preferably 15 to 90% still more preferably 10 to 100% preferably. The fall of the poor appearance of the thermoplastics constituent with which the rate of a graft of (A-1) is obtained at less than 10%, and impact strength-proof generates and is not desirable. On the other hand, fabrication nature is inferior when it exceeds 100%. Here, the above-mentioned rate of a graft (%) will be called for by the bottom type, if the methyl-ethyl-ketone insoluble daily dose in x and 1g (A-1) of components is set to y for the amount of rubber components in 1g (A-1) of components.

Rate (%) of graft =  $\{(y-x)/x\} \times 100$  [0014] Moreover, the limiting viscosity [eta] (it measures at 30 degrees C among a methyl ethyl ketone) of the matrix resin of rubber strengthening resin (A-1) is 0.3 - 0.7 dl/g especially preferably 0.2 to 0.9 dl/g still more

preferably 0.1 to 1.0 dl/g preferably. The thermoplastics constituent of this invention which was excellent in shock resistance and fabrication nature (fluidity) in limiting viscosity [eta] being the above-mentioned range is obtained. Here, matrix resin is resinous principles other than the graft-ized rubber component in a component (A-1), and the above-mentioned limiting viscosity [eta] is the value calculated by measuring methyl-ethyl-ketone extractives among components (A-1) according to a conventional method.

[0015] The rubber strengthening resin (A-1) of this invention can also be used not only combining a rubber strengthening resin (A-1) independent but combining (A-1) and the polymer (henceforth "A-3") which consists of a (b) component and a (c) component (\*\*). (\*\*) The lap (\*\*) of the (b) component in a polymer (A-3) is 48 - 100 % of the weight. Moreover, the amount of vinylcyanide compounds in a polymer (\*\*) (A-3) is less than 35 % of the weight. Therefore, a polymer (\*\*) (A-3) is clearly distinguished from the following copolymer (A-2) not only from the lap (\*\*) of the (b) component being 48 % of the weight or more but from this point. (\*\*) When the loadings of a polymer (A-3) and (A-1) (A-3) the total quantity are made into 100 % of the weight, it is 40 or less % of the weight preferably. In addition, the limiting viscosity [eta] (it measures at 30 degrees C among a methyl ethyl ketone) of a polymer (\*\*) (A-3) is 0.2 - 0.7 dl/g still more preferably 0.1 to 1.0 dl/g preferably.

[0016] As for a desirable combination of rubber strengthening resin (A-1), the following presentation is mentioned. However, the generic claim of this invention is not restrained by the following presentation.

\*\* Rubber strengthening resin / polymethylmethacrylate which carried out the graft polymerization of the 3 yuan copolymer \*\* methacrylic ester of the rubber strengthening resin / (meta) acrylic ester-styrene-acrylonitrile which carried out the graft polymerization of the rubber strengthening resin \*\* (meta) acrylic ester which carried out the graft polymerization of the metaacrylic ester [0017] On the other hand, the copolymer (A-2) of this invention is a copolymer which specified the amount of copolymerization of a vinylcyanide compound, and is a copolymer obtained by carrying out the polymerization of 65 - 50 % of the weight of at least one sort of monomer components chosen from the group of 35 - 50 % of the weight of vinylcyanide compounds, an aromatic series vinyl compound, acrylic ester (meta), an acid-anhydride system compound, and a maleimide system compound.

[0018] The same thing as the acrylic ester (b) and the monomer component (c) which are used for rubber strengthening resin (A-1) (meta) can be used for the above-mentioned vinylcyanide compound which constitutes an usable monomer component in a copolymer (A-2), an aromatic series vinyl compound, acrylic ester (meta), an acid-anhydride system compound, and a maleimide system compound.

[0019] The amount of copolymerization of the vinylcyanide compound in a copolymer (A-2) is 38 - 43 % of the weight still more preferably 36 to 45% of the weight preferably 35 to 50% of the weight. Chemical resistance is inferior in the amount of copolymerization

of the vinylcyanide compound in a copolymer (A-2) being less than 35 % of the weight, and on the other hand, when it exceeds 50 % of the weight, thermal stability is inferior. In addition, the amount of acrylic ester (meta) in a copolymer (A-2) is less than 48 % of the weight. Therefore, a copolymer (A-2) is clearly distinguished from the above-mentioned (\*\*) polymer (A-3) also from this point.

[0020] In addition, the limiting viscosity [eta] (it measures at 30 degrees C among a methyl ethyl ketone) of a copolymer (A-2) is 0.2 - 0.7 dl/g still more preferably 0.1 to 1.0 dl/g preferably. The AS resin which copolymerized the AS resin, 35 - 50 % of the weight of vinylcyanide compounds, and 5 - 20 % of the weight of methyl methacrylate which copolymerized 35 - 50 % of the weight of vinylcyanide compounds as a typical copolymer (A-2) is mentioned.

[0021] The above-mentioned rubber strengthening resin (A-1) for example, under existence of a \*\* rubber-like polymer (a) A monomer component (b) and (c) under existence of the approach of carrying out a polymerization and a \*\* rubber-like polymer (a) The polymerization of a monomer component (b) and a part of (c) is carried out, the polymerization of the remaining monomer components (b) and the (c) is carried out separately, and it is obtained by the manufacture approaches, such as the graft blending method which blends these. Moreover, the above-mentioned copolymer (A-2) and (\*\*) a polymer (A-3) are obtained in the approach of the \*\* above-mentioned \*\* or \*\* by the manufacture approach which does not use a rubber-like polymer (a).

[0022] Although it can manufacture according to a well-known emulsion polymerization, solution polymerization, a suspension polymerization, etc., the rubber strengthening resin (A-1), copolymer (A-2), and (\*\*) polymer (A-3) which are used for this invention are refined by drying after solidifying a product with a coagulant and usually rinsing the obtained powder, when it manufactures according to an emulsion polymerization. As this coagulant, mineral salt, such as a calcium chloride, magnesium sulfate, a magnesium chloride, and a sodium chloride, can be used. Moreover, acids, such as a sulfuric acid and a hydrochloric acid, can also be used as a coagulant.

[0023] A general thing can be used as a radical initiator at the time of a polymerization. As an example, a cumene hydroperoxide, diisopropylbenzene hydroperoxide, potassium persulfate, azobisisobutyronitril (azobisisobutyronitril), benzoyl peroxide, lauroyl peroxide, t-butyl peroxy laurate, t-butyl par OKISHIMONO carbonate, etc. are mentioned.

[0024] Furthermore, in rubber strengthening resin (A-1) or a copolymer (A-2), a functional-group content vinyl system monomer can also be copolymerized. As this functional group, an epoxy group, a hydroxyl group, a carboxylic-acid radical, the amino group, an amide group, an oxazoline radical, etc. are mentioned. As a concrete functional-group content vinyl system monomer, glycidyl methacrylate, glycidyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxyethyl acrylate, acrylamide, an acrylic acid, a methacrylic acid, vinyl oxazoline, etc. are mentioned. By copolymerizing these functional-group content vinyl system monomers, interface adhesion (compatibility) with other resin can be raised. It is 0.5 - 12 % of the weight still more preferably 0.1 to 15% of

the weight preferably the amount of copolymerization of these functional-group content vinyl system monomers, or (A-1) (A-2) in a component.

[0025] (A) thermoplastics component of this invention uses rubber strengthening resin (A-1) or rubber strengthening resin (A-1), and a copolymer (A-2) as a principal component. Here the blending ratio of coal of rubber strengthening resin (A-1) and a copolymer (A-2) Rubber strengthening resin (A-1) preferably 50 to 100% of the weight 60 - 90 % of the weight, A copolymer (A-2) is 35 - 15 % of the weight [however, (A-1)+(A-2) =100 % of the weight] still more preferably 40 to 10% of the weight preferably 50 to 0% of the weight 65 to 85% of the weight still more preferably. (A-1) The laser marking nature which a component makes the purpose of this invention at less than 50 % of the weight is not inferior and desirable.

[0026] The amount of the vinylcyanide compound which is contained in (A) thermoplastics component of this invention and by which the polymerization was carried out is 12 - 25 % of the weight especially preferably ten to 28% of the weight still more preferably eight to 30% of the weight preferably one to 33% of the weight. (A) Thermal stability is inferior, when less than 1 % of the weight of chemical resistance is [ the amount of vinylcyanide compounds in a component ] insufficient and it, on the other hand, exceeds 33 % of the weight.

[0027] In addition, the amount of the acrylic ester (meta) which is contained in (A) thermoplastics component of this invention and by which the polymerization was carried out is 38 - 43 % of the weight especially preferably 35 to 45% of the weight still more preferably 20 to 50% of the weight preferably. When less than 20 % of the weight of laser marking nature is [ the amount of the acrylic ester (meta) by which the polymerization was carried out ] insufficient and it, on the other hand, exceeds 50 % of the weight, thermal resistance and chemical resistance are inferior.

[0028] (A) As for the combination with a desirable thermoplastics component, the following presentation is mentioned. However, the generic claim of this invention is not restrained by the following presentation.

\*\* ABS plastics which copolymerized the methyl methacrylate (the amount of copolymerization acrylonitrile: 5 - 10 % of the weight)

\*\* The ABS plastics/AS resin which copolymerized the methyl methacrylate (the amount of copolymerization acrylonitrile: 40 % of the weight)

\*\* The AS resin which copolymerized the ABS plastics/methyl methacrylate which copolymerized the methyl methacrylate (the amount of copolymerization acrylonitrile: 5 - 10 % of the weight)

[0029] Next, the (B) components used for this invention are black system compounds, such as carbon black. (B) As a component, black system compounds, such as carbon black, black iron oxide, black titanium oxide, and a graphite, can be used. If the (B) component which is the above-mentioned black system compound is expressed with a wavelength-reflection factor curve, a reflection factor will be 5% or less of thing preferably 10% or less to all fields with a wavelength of 400-700nm. That is, if it is the compound



which absorbs the light of the wavelength of all these 400-700nm fields, it can be used as a (B) component of this invention.

[0030] (B) As carbon black of a component, both acetylene black channel black furnace black KETCHIEN black, etc. are usable. 10-80nm of desirable particle size of carbon black is 12-40nm still more preferably. The dispersibility in the inside of resin has the good one where particle size is smaller, and laser marking color enhancement is good. Moreover, a desirable specific surface area of carbon black is [ 35-300m<sup>2</sup> / 100g, and desirable pH of 20-1,500m<sup>2</sup> / g, and desirable oil absorption ] 2-10.

[0031] Moreover, black iron oxide is Fe<sub>3</sub>O<sub>4</sub>. FeO-Fe<sub>2</sub>O<sub>3</sub> It is the black ferric acid ghost expressed. Although a desirable particle size of black iron oxide is 0.4-0.6 micrometers and the shape of a globular shape and a cube and every needlelike all can be used for it as the configuration still more preferably 0.3-0.8 micrometers, its shape of a cube is desirable. Furthermore, black titanium oxide is a compound obtained by returning a titanium dioxide. 0.1-60 micrometers of desirable particle size of black titanium oxide are 1-20 micrometers still more preferably.

[0032] A color, an organic pigment, etc. can also be blended with the thermoplastics constituent for laser marking of this invention. The laser marking nature which presents a chromatic color is obtained by using together these colors organic pigments, etc. and black system compounds. If the above-mentioned color, organic pigment, etc. are expressed with a wavelength-reflection factor curve, in a 400-700nm wavelength field, reflection factors will be 40% or more of field, and the color and organic pigment which have 50% or more of field preferably partially. By selecting these colors and organic pigments appropriately, yellow, red, blue, and which green and purple chromatic color can be colored to \*\*\*\*. The color of the color and organic pigment to blend makes an exposure part color fundamentally at the time of a laser light exposure.

[0033] As an usable color, nitroso dye, nitro dye, azo dye, stilbene azo dye, a keto imine color, triphenylmethane dye, xanthene dye, acridine dye, quinoline dye, methine dye, thiazole dye, an indamine color, azine dye, an oxazine color, thiazine dye, sulfur dye, aminoketone dye, anthraquinone dye, indigoid dye, etc. are mentioned to this invention.

[0034] As an example of these colors Mordant Green 4 and Disperse Yellow 14 and Disperse Yellow 31 Acid Yellow 2 Direct Yellow 59 and Basic Yellow 2 Basic Orange 23 Direct Orange 71 Direct Red 28 Acid Red 52 Solvent Blue 22 Acid Blue 59 Mordant Blue 10 and Acid Blue 45 Vat Blue 41, toluidine MARUN, Permanent Red AG, Hansa Yellow G, Hansa Yellow 10G, benzidine orange 2G, etc. are mentioned.

[0035] Moreover, although what is generally used can be used as an organic pigment, the configured metal has desirable things, such as calcium, nickel, iron, barium, sodium, copper, molybdenum, cobalt, manganese, zinc, titanium, magnesium, and a potassium, especially. As a concrete organic pigment, Watchung Red (calcium), green gold (nickel), and pigment Green B (Fe), pigment scarlet 3B (Ba), Fast Sky Blue (Ba), Phthalocyanine Green (Fe), a copper phthalocyanine blue (Cu), brilliant carmine 6B (calcium), Bordeaux 10B (Na), Lithol Red R (Na), Lake Red D (Na), brilliant scarlet G (calcium), manganese

violet (Mn), cobalt violet (Co), etc. are mentioned. In addition, the element contained in an organic pigment was shown in the parenthesis after these names.

[0036] In the thermoplastics constituent for laser marking of this invention, as a device in which a chromatic color is colored, although it still is not clear, it thinks as follows. That is, in the case of carbon black or a graphite, the black system compound of the (B) component blended into (A) thermoplastics component absorbs laser light, and the carbon which exists in an exposure part evaporates. In this phase, the black component in an exposure part is lost, or it decreases. Since the color, organic pigment, etc. which, on the other hand, has the chromatic color which existed in the exposure part do not absorb laser light, it exists in an exposure part as it is, and makes an exposure part color the chromatic color of the origins, such as a color and an organic pigment. Moreover, as explanation of other devices, the (B) component absorbs laser light and carries out thermal conversion of the light. Since refractive indexes differ, black does not become but the chromatic color of a color and the organic pigment origin is made to color in the foaming part and the part which is not irradiated according to the heat to generate decomposing and making the acrylic ester (meta) component in a thermoplastics constituent foam. The (B) component needs to absorb laser light and, on the other hand, it is necessary for a color, an organic pigment, etc. not to absorb the wavelength of laser light so that such a coloring device may show.

Moreover, when black titanium oxide is used, at the time of an optical exposure, black titanium oxide oxidizes and presents the white of a titanium dioxide. Therefore, the color of the color and the organic pigment origin which exists in this part can be recognized.

[0037] the blending ratio of coal in the thermoplastics constituent for laser marking of this invention -- the (A) thermoplastics component 100 weight section -- receiving -- the (B) component -- 0.01 - 5 weight section -- desirable -- 0.02 - 3 weight section -- further -- desirable -- 0.03 - 2 weight section -- it is 0.05 - 1 weight section especially preferably. (B) Even if the blending ratio of coal of a component is inferior in coloring of laser marking and exceeds 5 weight sections on the other hand under in the 0.01 weight section, laser marking coloring and shock resistance are inferior.

[0038] The thermoplastics constituent for laser marking of this invention is irradiating the mold-goods front face with laser light, and it is possible to make \*\*\*\* color a chromatic color into an exposure part. Here, as a laser light, they are helium-Ne, Ar laser, and CO<sub>2</sub>. Solid state laser, such as gas laser, such as laser and an excimer laser, and an YAG laser, semiconductor laser, dye laser, etc. are mentioned, and it is CO<sub>2</sub> especially. Laser, an excimer laser, and an YAG laser are desirable. The wavelength of YAG laser light is 1,054nm.

[0039] If the shaping front face of the thermoplastics constituent for laser marking of this invention is irradiated with laser light, a laser light exposure part will be a foaming phenomenon by laser light exposure, and will usually rise a little from a non-irradiated part. Although the desirable climax height of this exposure part is about 1-100 micrometers, about 10-80 micrometers has laser marking coloring and clear recognition of an exposure (alphabetic character) part, and are desirable. Moreover, it is also possible to produce the

mold goods for Braille points using this alphabetic character height. In addition, a foaming phenomenon arises also inside a resin front face by laser light exposure with a natural thing. [0040] If needed, to the thermoplastics constituent for laser marking of this invention, it is independent one sort, or two or more sorts of fillers, such as a glass fiber, a carbon fiber, straw SUTONAITO, talc, a mica, a glass flake, a milled fiber, a zinc oxide whisker, and a potassium titanate whisker, can be used together to it. Rigidity can be given to the thermoplastics constituent for laser marking of this invention by blending these fillers. Moreover, lusterless nature can be given to the thermoplastics constituent for laser marking of this invention by blending talc etc. As a desirable configuration of the above-mentioned glass fiber and a carbon fiber, the diameter of fiber is 6-20 micrometers, and fiber length is 30 micrometers or more. The loadings of these fillers are 2 - 30 weight section preferably [ it is desirable and ] to 1 - 50 weight section and a pan to the (A) thermoplastics component 100 weight section used for this invention. If the loadings of a filler exceed 50 weight sections, laser marking nature, a mold-goods appearance, and practical use shock resistance will be spoiled.

[0041] Moreover, additives, such as a well-known coupling agent, a weathering agent, an antioxidant, a plasticizer, lubricant, coloring agents other than the (B) component, an antistatic agent, and silicone oil, can be blended with the thermoplastics constituent for laser marking of this invention. Among these, as a weathering agent, the organic compound of the Lynn system and a sulfur system and the organic compound containing a hydroxyl group are desirable. Moreover, the sulfonate which has a polyether and an alkyl group is mentioned as an antistatic agent. The desirable loadings of these additives are 0.5 - 5 weight section preferably to 0.1 - 10 weight section and a pan to the (A) thermoplastics component 100 weight section used for this invention.

[0042] Furthermore, according to the application demanded, other polymers, such as other thermoplastics, thermosetting resin, etc., can be blended with the thermoplastics constituent for laser marking of this invention. Here, as other polymers, a polycarbonate, polyethylene, polypropylene, polyamide, polyester, polysulfone, polyether sulphone, polyphenylene sulfide, liquid crystal polymer, polyvinylidene fluoride, polytetrafluoroethylene, and styrene-vinyl acetate copolymer, a polyamide elastomer, a polyamidoimide elastomer, a polyester elastomer, a polyether ester amide, phenol resin, an epoxy resin, novolak resin, etc. are mentioned. In these, if a polyamide, polyethylene, polypropylene, etc. are blended, laser marking nature coloring can be made more into \*\*\*\*. these -- others -- the loadings of a polymer -- the (A) thermoplastics component 100 weight section -- receiving -- desirable -- the 1 - 150 weight section -- it is the 5 - 100 weight section still more preferably. Moreover, it is possible to give permanent antistatic nature by blending a polyamide elastomer, a polyether ester amide, etc. among a polymer besides the above. Desirable loadings are 2 - 20 weight section preferably to 1 - 30 weight section and a pan to the (A) thermoplastics component 100 weight section.

[0043] Furthermore, a flame retarder can also be blended in order to give fire retardancy to the thermoplastics constituent for laser marking of this invention. independent [ in a

halogen system compound, an organic phosphorus system compound, a nitrogen system compound, a metal hydroxylation compound, an antimony compound, etc. ] as a flame retarder -- or it can be used together and used.

[0044] Among these, as a halogen system compound, the oligomer (the end may be closed by the epoxy group, tribromophenol, etc.) of tetrabromobisphenol A and tetrabromobisphenol A, bromination polystyrene, post-bromination polystyrene, bromination polycarbonate oligomer, TORIBUROMO phenoxy ethane, chlorination polystyrene, an aliphatic series chlorine compound, etc. are mentioned. Especially, the oligomer of tetrabromobisphenol A is desirable (desirable molecular weight is 1,000 to about 6,000). Moreover, halogen atom concentration, such as a bromine in a halogen system compound, is 45 - 60 % of the weight still more preferably 30 to 65% of the weight preferably.

[0045] Moreover, as an organic phosphorus system compound, the oligomer of triphenyl phosphate, trixylenyl phosphate, tricresyl phosphate, TORIKISHIRE nil thio phosphate, a hydroquinone screw (diphenyl phosphate), resorcinol bis(diphenyl phosphate), a resorcinol screw (dixylenyl phosphate), and triphenyl phosphate etc. is mentioned. Especially, triphenyl phosphate, trixylenyl phosphate, and a REZOSHI Norian screw (xylenyl phosphate) are desirable. The desirable Lynn concentration of an organic phosphorus system compound is 6 - 25 % of the weight still more preferably four to 30% of the weight. Furthermore, as a nitrogen system compound, they are triazine, a melamine, etc. Furthermore, a magnesium hydroxide, an aluminum hydroxide, etc. can be used as a metal hydroxylation compound. Furthermore, an antimony trioxide, antimony pentoxide, etc. can be used as an antimony compound.

[0046] the (A) thermoplastics component 100 weight section by which the loadings of the above flame retarder are used for this invention -- receiving -- desirable -- 1 - 50 weight section -- further -- desirable -- 2 - 30 weight section -- it is 5 - 25 weight section especially preferably. In under 1 weight section, the grant effectiveness of fire retardancy [ loadings / of a flame retarder ] is inadequate, and on the other hand, when 50 weight sections are exceeded, shock resistance and laser marking nature are inferior.

[0047] The thermoplastics constituents for laser marking of this invention are various extruders, a Banbury mixer, a kneader, a roll, etc., and can be preferably obtained by kneading each component in 160 degrees C - 300 degrees C. After facing kneading, and carrying out package kneading of each component and kneading the component of arbitration, the multistage division kneading method for adding and kneading the remaining components is also employable. The desirable kneading method is the approach of performing with an extruder, and is desirable especially as an extruder. [ of a co-rotating twin screw extruder ] In addition, in order to prepare the thermoplastics constituent for laser marking of this invention It cannot be overemphasized that melting kneading of the (B) component may be carried out at the (A) component which blended the component (A-1) and the component (A-2), and was obtained, or melting kneading of (A-1), (A-2), and the (B) component may be beforehand carried out on a multistage story with a rate of

coincidence or arbitration.

[0048] The resin constituent for laser marking of this invention can be fabricated to various mold goods by injection molding, sheet extrusion molding, the vacuum forming, variant extrusion, foaming, etc. By the above-mentioned fabricating method, mold goods, such as carbon buttons, such as OA product, home electronics, and a car application, housing, and a switch, can be obtained. Moreover, it can be used for a threshold, a window frame, the charge of railing, etc. as a building material. A clear chromatic color can be made to color by carrying out the laser light exposure of these product front faces. Moreover, since the alphabetic character part made to color by laser marking is excellent in weatherability and excels the printed alphabetic character part also in abrasion resistance, it is more desirable than printing practically for whether your being Haruka.

[0049]

[Example] Although an example is given and this invention is explained still more concretely hereafter, this invention is not restrained at all by the following examples, unless the summary is exceeded. In addition, among an example, the section and especially % are weight criteria, unless it refuses. Moreover, various kinds of parameters in an example followed below.

[0050] Since the mean particle diameter of a mean-particle-diameter particulate material checked with the electron microscope that the particle diameter of the latex beforehand compounded in the state of emulsification showed the particle diameter of the particulate material in resin as it is, it measured the particle diameter of the particulate material in a latex with light scattering measurement. measuring equipment -- the product made from Otsuka Electron, and LPA-3100 -- using it -- 70 times addition -- KYUMURANTO -- particle diameter was measured using law.

[0051] Precise-weighing extraction of the 1g of the rate samples of a graft is carried out, the shaking of the acetone 20cc was added and carried out to this for 10 hours, after that, it separated into extractives and insoluble matter using the centrifugal separator of rotational frequency 20,000rpm, insoluble matter was dried with the vacuum dryer, and insoluble matter (X) was obtained. On the other hand, the amount of rubber (R) in insoluble matter (X) was computed from the polymerization presentation and the polymerization invert ratio, and it asked for the rate of a graft (%) from the degree type.

Rate of graft =  $\frac{[(X)-(R)]}{100} \times 100 / (R)$

Limiting viscosity [eta]

In the case of the copolymer (A-2) and the polymer (\*\*) (A-3), the sample was dissolved in the methyl ethyl ketone which is a solvent as it was, and it measured that to which the above-mentioned extractives were dried using the vacuum dryer in the case of rubber strengthening resin (A-1) with the Ubbelohde viscometer according to 30-degree C temperature conditions again.

[0052] Izod impactive strength (IMP)

ASTM Based on D256, it measured by the thickness of 1/4", and the test condition 23 degrees C and with a notch.

Japanese Publication number : 2000-212378A

Fluidity (melt flow rate)

ASTM It measured according to D1238. Measurement temperature is 220 degrees C and a load is 10kg.

Heat deflection temperature ASTM It measured according to D648.

[0053] Tabular mold goods were produced for the laser marking nature thermoplastics constituent using the injection molding machine. Laser marking of the mold-goods front face was carried out using the laser marker made from curl BAZERU (star mark 65W; YAG laser light). By irradiating, the color enhancement of the part to color, recognition nature, and clearness were judged visually.

O; fitness (when presenting clear alphabetic character coloring with good recognition nature)

\*\*; good (when it is inferior any of visibility and recognition nature they are)

x; it is inferior (when visibility and recognition nature are inferior).

[0054] Combustion test (fire retardancy)

UL-94 It was based on V test. Thickness is 1.6mm. V-2 shows V-2 ranks in a perpendicular trial, and HB shows the HB rank in a level trial.

Surface specific resistance ASTM (electrical property) It measured according to D257. Measuring conditions are 23 degrees C and 50%RH, and a unit is omega.

[0055] Tabular mold goods were produced for the chemical-resistant thermoplastics constituent using the injection molding machine. Thickness is 1.6mm. 1/4" of the mold goods was fixed to the ellipse jig, and it was left for three days, applying drugs on mold goods. Then, a surface crack condition was judged visually and it asked for the critical strain using the contrast table. In addition, the hair liquid and the hand cream were used as drugs.

O; fitness (0.8 or more critical strains)

\*\*; good (critical strains 0.4-0.7)

x; it is inferior (0.3 or less critical strain).

[0056] an example -- one - seven -- a comparison -- an example -- one - four -- rubber -- strengthening -- resin (A-1) -- preparation -- < (A-1-\*\*) -- [ -- rubber -- strengthening -- resin (MMA copolymerization ABS plastics) -- preparation -- ] -- > -- an agitator -- having had -- content volume -- seven -- l. -- glass -- a flask -- The temperature up was carried out adding and stirring the ion-exchange-water 100 section, the sodium dodecylbenzenesulfonate 1.5 section, the t-dodecyl mercaptan 0.1 section, the (Polybutadiene a) 15 section (solid content conversion), the styrene 5 section, the acrylonitrile 5 section, and the methyl-methacrylate 10 section. When temperature amounted to 45 degrees C, the activator water solution which consists of the ethylenediaminetetraacetic acid sodium 0.1 section, the ferrous-sulfate 0.003 section, the sodium formaldehyde sulfoxylate and 2 hydrate 0.2 section, and the ion-exchange-water 15 section, and the diisopropylbenzene hydroperoxide 0.1 section were added, and the reaction was continued for 1 hour.

[0057] Then, the INKURE mental polymerization component which consists of the

ion-exchange-water 50 section, the sodium dodecylbenzenesulfonate 1 section, the t-dodecyl mercaptan 0.1 section, the diisopropyl hydroperoxide 0.2 section, the styrene 10 section, the acrylonitrile 5 section, and the methyl-methacrylate 50 section was continuously added over 3 hours, and the polymerization reaction was continued. After addition termination, after continuing stirring further for 1 hour, the 2,2-methylene bis-(4-ethylene-6-t-butylphenol) 0.2 section was added, and the resultant was picked out from the flask. After solidifying the latex of a resultant in the calcium chloride 2 section and rinsing a resultant well, it dried at 75 degrees C for 24 hours, and white powder was obtained. The polymerization invert ratios was [ the limiting viscosity of the rate of a graft ] 0.40 dl/g 40% 98.5%.

[0058] The polymerization of the MMA copolymerization ABS plastics (A-1-\*\*) was carried out using the same polymerization method as the <(A-1-\*\*) preparation [ of [rubber strengthening resin (MMA copolymerization ABS plastics) ] ]> above. The presentation of this resin was butadiene rubber / styrene / methyl-methacrylate / acrylonitrile =20/20/55/5(%). The rate of a graft was 50% and limiting viscosity was 0.50 dl/g.

<(A-1-\*\*) (ABS plastics for comparison) > presentation; butadiene rubber / styrene / acrylonitrile =30/50/20 (%)

rate of graft; -- 60% limiting viscosity; -- 0.35 dl/g [0059] The preparation <A-2-\*\* (AS resin)> presentation of a copolymer (A-2); styrene / acrylonitrile =60 / 40 (%)

limiting viscosity; -- 0.50 dl/g<A-2-\*\* (AS resin) > presentation; -- styrene / acrylonitrile =62 / 38 (%)

limiting viscosity; -- 0.45 dl/g<A-2-\*\* (AS resin) > presentation; -- styrene / acrylonitrile =55 / 45 (%)

limiting viscosity; -- 0.45 dl/g<A-2-\*\* (AS resin for comparison) > presentation; -- styrene / acrylonitrile =80 / 20 (%)

limiting viscosity; -- 0.30 dl/g<A-2-\*\* (AS resin for comparison) > presentation; -- styrene / acrylonitrile =20 / 80 (%)

limiting viscosity; -- preparation <A-3 (MMA copolymerization AS resin)> presentation; of a 0.30 dl/g copolymer (A-3) -- styrene / acrylonitrile / MMA=35/15/50 (%)

Limiting viscosity; 0.40 dl/g [0060] (B) preparation B- of a component -- 1; carbon black B-2; black-iron-oxide B-3; -- black titanium oxide [0061] The preparation > polyether ester amide of a polymer besides preparation [ of other components ] <; a nylon 6 block / polyethylene oxide block =50 / 50 (%)

oligomer [ of <flame-retarder> tetrabromobisphenol A ]; -- an end -- tribromophenol -- closure, bromine concentration =56%, and molecular weight = -- about 2,000 [0062] A color and <organic pigment> pigment \*\*;Mordant Green 4 pigment \*\*;Direct Yellow 31 pigment \*\*;Direct Red 28 [0063] At a rate which indicated the polymer and additive of the preparation (A) component of a thermoplastics constituent, the (B) component, and others to Table 1, melting kneading was carried out using the extruder under 220-240-degree C temperature conditions, and the evaluation sample was obtained with injection molding.

The example of this invention was shown in Table 1.

[0064] The shock resistance to which any thermoplastics constituent colors good white alphabetic character coloring or a chromatic color, and can be equal to practical use in laser marking nature evaluation was shown. Moreover, a moldability and chemical resistance were also what can fully be equal to practical use. Moreover, the thermoplastics constituent of this invention containing a polyether ester amide showed the good electrical property (example 6), and the thing containing a flame retarder showed good fire retardancy (example 7). In addition, any thermoplastics constituent of a base color is black or gray. On the other hand, the example 1 of a comparison is the case of under the loadings that the amount of copolymerization of the vinylcyanide compound in the copolymer (A-2) of this invention specifies to this invention, and is inferior in practical shock resistance. The example 2 of a comparison is the case of under the loadings that the amount of copolymerization of the acrylic ester (meta) of the rubber strengthening resin (A-1) of this invention specifies to this invention, and good laser marking nature and chemical resistance are not obtained. The example 3 of a comparison is the case where the (B) component exceeds the loadings specified to this invention, and laser marking coloring is not obtained but it is inferior also in practical shock resistance. Rubber strengthening resin (A-1) is under the loadings specified to this invention, and the example 4 of a comparison is the case where there is no (B) component, and laser marking coloring is not obtained but it is inferior also in practical shock resistance. The example 5 of a comparison is the case where the amount of copolymerization of the vinylcyanide compound in a copolymer (A-2) exceeds the loadings specified to this invention, and thermal resistance and shock resistance are inferior in it, and it is inferior in the thermal stability at the time of shaping.

[0065]

[Table 1]



	実施例							比較例				
	1	2	3	4	5	6	7	1	2	3	4	5
<b>配合処方 (部)</b>												
(A) ; A-1-① (MMA共重合ABS)	70	-	70	-	70	70	-	70	-	-	20	60
A-1-② (MMA共重合ABS)	-	65	-	100	-	-	65	-	-	70	-	-
A-1-③ (比較用ABS)	-	-	-	-	-	-	-	-	65	-	-	-
A-3 (MMA-AN-St)	-	-	10	-	-	-	-	-	-	-	-	-
A-2-① (AS)	30	-	-	-	30	30	-	-	-	30	80	-
A-2-② (AS)	-	35	-	-	-	-	35	-	35	-	-	-
A-2-③ (AS)	-	-	20	-	-	-	-	-	-	-	-	-
A-2-④ (比較用AS)	-	-	-	-	-	-	-	30	-	-	-	-
A-2-⑤ (比較用AS)	-	-	-	-	-	-	-	-	-	-	-	40
<b>(A) 成分組成 (%) ;</b>												
(メタ) アクリル酸エステル	42	37	47	55	42	42	37	42	0	39	12	36
シアン化ビニル化合物	19	16	19	5	19	19	16	19	26	16	34	38
<b>(B) ; B-1</b>												
B-2	0.2	-	0.1	0.2	-	0.2	-	0.1	0.3	10	-	0.2
B-3	-	0.1	-	-	0.2	-	0.1	-	-	-	-	-
<b>その他 ; ポリエーテルエステルアミド</b>												
難燃剤	-	-	-	-	-	15	-	-	-	-	-	-
顔料①	-	-	-	0.3	-	-	15	-	-	-	-	-
顔料②	-	-	-	-	0.2	-	-	-	-	-	-	-
顔料③	-	-	-	-	-	-	0.3	-	-	-	-	-
<b>熱可塑性樹脂組成物の評価</b>												
アイゾット衝撃強度 (J/m)	178	198	178	228	128	248	108	58	268	48	48	48
流動性 (g/10min)	20	21	20	16	24	25	30	35	18	18	25	39
熱変形温度 (°C)	89	89	80	87	92	86	86	89	92	89	90	82
レーザーマーキング性	○	○	○	○	○	○	○	○	△	×	×	△
文字色	白	白	白	緑	黄	白	赤	白	黒	白	×	白
難燃性	HB	HB	HB	HB	HB	HB	V-2	HB	HB	HB	HB	HB
電気特性 (Ω)	>1B16	-	-	-	-	-	1B11	-	-	-	-	-
耐薬品性 ; ヘアーリキッド	○	○	○	○	○	○	○	×	△	○	○	○
ハンドクリーム	○	○	○	○	○	○	○	△	○	○	○	○

[0066]

[Effect of the Invention] The constituent for laser marking of this invention can color red, yellow, and which green chromatic color to \*\*\*\*, and is excellent also in practical shock resistance, thermal resistance, fabrication nature, and chemical resistance with the exposure of laser light, and useful for the application of building materials, such as carbon buttons, such as OA product, home electronics, and a car application, housing, a switch, a threshold, a window frame, and a charge of railing, etc.

[Translation done.]

